

SEPARATIONS

Hydrogen Transport through Tubular Membranes of
Palladium-Coated Tantalum and Niobium

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Palladium-based membranes have been used for decades in hydrogen extraction because of their high permeability and good surface properties and because palladium, like all metals, is 100% selective for hydrogen transport. We describe experiments with hydrogen-extraction membranes made of palladium-coated niobium and tantalum heat-exchanger tubes. The cost was about \$45/ft of $\frac{3}{8}$ in. tubular membrane, and the fluxes were as high as $0.00147 \text{ mol/m}^2 \text{ s Pa}^{1/2}$ at 420°C . The main transport resistance is in the refractory metal substrate. Durability tests showed a 15% reduction in flux for 31 days of continuous membrane operation. Assuming durability is maintained for at least 1 year, this price and flux should allow competitive application for hydrogen recovery in petrochemical plants and for membrane reactors.

Introduction

Palladium membranes have been used for decades to provide very pure hydrogen for semiconductor manufacture, fuel cells, and laboratory use. Palladium combines excellent hydrogen transport and discrimination properties with resistance to high temperatures, corrosion, and solvents. Further, palladium is easily formed into tubes that are easily fabricated into hydrogen extraction units^{1,2} and palladium surfaces are not readily poisoned by carbon monoxide, steam, and hydrocarbons.^{1,3,27} These properties would make palladium membranes very attractive for use with petrochemical gases except that palladium and its alloys are expensive and soft. Membrane units must employ thick-walled tubes costing \$3000/ft² or more. Further, the thick wall lowers the hydrogen flux since flux is inversely proportional to membrane thickness. Thus, despite their advantages, palladium-alloy membranes are usually too expensive for large-scale hydrogen recovery and membrane reactors.

Developmental History of Composite Metal Membranes

As Figure 1 shows, several low-cost refractory metals have greater hydrogen permeabilities than palladium. These metals, including niobium, tantalum, and vanadium, are also stronger than palladium and are easily fabricated into tubes and other useful shapes. Thin-walled tubes of these metals would show very high hydrogen fluxes at a fraction of the cost of palladium, but until recently their poor surface properties reduced transport dramatically.⁴⁻¹³

In 1967, Makrides et al. at Harvard University⁴ patented a hydrogen-extraction membrane where a refractory metal was coated with palladium to facilitate hydrogen ingress and egress and to prevent oxidation of the refractory metal surfaces. The resulting mem-

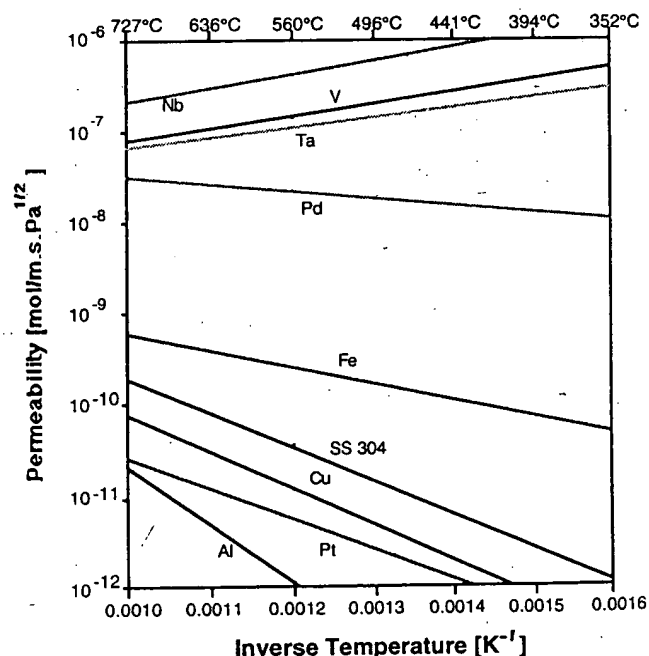


Figure 1. Hydrogen permeabilities of selected metals.

brane showed greater hydrogen transport than with palladium or its alloys, was strong, produced 100% pure hydrogen, and had a high tolerance to pinhole defects in the coat. Although the coat was not continuous, selectivity remained 100% because the nonporous substrate blocked non-hydrogen gas transport that penetrated defects in the coat.

Makrides et al.'s membranes achieved limited application though because the coating process, palladium vapor deposition at high vacuum, was expensive and deficient. Vapor deposition does not coat inside tubes, the preferred extractor configuration, and generally retains significant surface transport resistance. Hydrogen transport, while higher than with palladium, was one-tenth that predicted from the data in Figure 1. Makrides et al.'s vapor-coated membranes found use only in the nuclear industry where the high cost is offset

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by the membranes' high flux and durability. A palladium-coated alloy membrane worked for over 10 000 h continuously, removing hydrogen from metal-cooled nuclear reactor fluids,⁹ and palladium-coated zirconium has been tested successfully for removing embrittling deuterium from CANDU reactor bundles.¹⁴

More recently, Hsu and Buxbaum patented a lower-cost electroless deposition process for applying a uniform palladium coat to refractory metals, even inside tubes.¹⁵ Amano et al.¹⁹ demonstrated membranes of a non-embrittling vanadium alloy which extends the range of coated-membrane operation, in theory, down to room temperature. Also, flux measurements with coated tantalum, niobium, and zirconium disks have generally corroborated the predictions in Figure 1 and corroborated the predicted 100% hydrogen selectivity.^{10,16} The permeance of a 0.25 mm wall niobium tube at 420 °C was found to be 0.0007 mol/m² s Pa^{1/2}, much higher than that for a Ube polymer membrane operating at 100 °C and these pressure drops.¹⁶ However, the predicted cost was \$500/ft², more than double that for polymeric membranes.³¹

Background to Hydrogen Transport in Metals

Hydrogen transport through metals has been studied extensively.^{11,13,17,18} Since hydrogen molecules dissociate into atoms to diffuse through metals, transport is calculated from the atomic flux. Fick's first law describes the flux of hydrogen atoms through a homogeneous phase as:

$$N_H = -D_M(\Delta C_H/\delta_M) \quad (1)$$

where N_H is the atomic flux, D_M is diffusivity, ΔC_H is the change in hydrogen atom concentration across the membrane, and δ_M is the membrane thickness. C_H is related to the partial pressure of hydrogen in equilibrium with the metal, correlated for example by

$$C_H = K_S(P^{1/2}) \quad (2)$$

where K_S is the Sieverts constant and P is the partial pressure of hydrogen in equilibrium with the metal. The power of $1/2$ comes from the dissociation of hydrogen molecules into twice as many atoms at low concentration.

We now calculate the flux of hydrogen molecules, N , in terms of pressure using eq 1 and 2. Since the flux of molecules is half the flux of atoms:

$$\begin{aligned} N &= (D_M K_S / 2\delta_M) \Delta P^{1/2} \\ &= \mathcal{P}_M \Delta P^{1/2} / \delta_M \end{aligned} \quad (3)$$

The term \mathcal{P}_M above is called the metal permeability,

$$\mathcal{P}_M = D_M K_S / 2 \quad (4)$$

a pressure-independent constant for a given metal at low hydrogen contents. Two derived quantities, the "permeance" and the "total resistance to transport", are respectively the flux divided by the pressure driving force and the inverse of this number. These numbers are related to the average permeability, \mathcal{P}

$$\text{permeance} \equiv N/\Delta P^{1/2} = \mathcal{P}/\delta \quad (5)$$

$$R_{\text{Tot}} \equiv \Delta P^{1/2}/N = \delta/\mathcal{P} \quad (6)$$

In a multilayered membrane the total transport resistance of a membrane, R_{Tot} , is the sum of the resistance in each layer ($\sum \delta_M/\mathcal{P}_M$) plus the effective resistance caused by gas-phase diffusion.⁶

Permeabilities of the refractory metals vanadium, tantalum, zirconium, and niobium are so large that until recently they were inferred only from diffusivity and low concentration solubility coefficients via eq 4. These values are shown in Figure 1 along with experimental values for several nonrefractory metals. Recent measurements have confirmed the prediction that these metals are significantly more permeable than palladium.^{10,16} Figure 1 shows \mathcal{P}_M for some metals increasing with decreasing temperature. This temperature dependence occurs when hydrogen absorption is more exothermic than the activation energy for diffusion is endothermic, e.g., with palladium-coated zirconium.¹⁰

In polymer and porous ceramic membranes, flux is proportional to ΔP , not to $\Delta P^{1/2}$ as with metal membranes. Because of this, metal membranes are more attractive at low hydrogen pressures. This is seen by approximating for $\Delta P^{1/2}$ from the derivative with respect to P ,

$$P^{1/2} \approx \Delta P / 2\bar{P}^{1/2}$$

where \bar{P} is the average hydrogen partial pressure. Combining this with eq 3 for flux through a metal membrane

$$N \approx (\mathcal{P}_M / 2\delta_M \bar{P}^{1/2}) \Delta P$$

flux per pressure drop decreases with increasing hydrogen pressure. In a polymer or ceramic this permeance is measured in barrers and is fairly pressure independent.

High hydrogen concentrations tend to decrease a metal's diffusivity but increase its Sieverts constant.^{17,20} The hydrogen diffusivity decreases because the nearest-neighbor sites for hydrogen atom jumps become filled.²⁰ Because hydrogen concentration increases with decreasing temperature, this effect tends to flatten the temperature dependence of the hydrogen permeability. The Sieverts constant rises with increasing concentration because the hydrogen atoms attract. The net effect is that fluxes are effected little but often vary from the pressure to the $1/2$ expectation. Palladium-coated tantalum and niobium disks show permeabilities similar to Figure 1, but the temperature effect is flattened.¹⁶ This paper will discuss pressure effects.

Gas-phase transport resistance, surface resistance (dissociation/recombination), and interface effects can also affect transport,^{13,21,22,27} and several modifications of eq 3 include these resistances.^{7,21,22} With proper coating, though, interface resistance can be removed almost completely.^{13,23} Similarly, dissociation on palladium presents little transport resistance even at temperatures as low as 325 °C¹⁰ unless fouling is present. Palladium is fairly immune to surface poisoning,²⁸⁻³⁰ but since these membranes are so permeable, they may foul with impurity concentrations that would go unnoticed with homogeneous palladium or alloys. Also, because the membranes are extremely permeable and are 100% selective, gas-phase mass transport resistance can appear at flows and geometries which would be inconceivable with other membranes.

The experimental setup is shown in Figures 2 and 3. We use tubular membranes rather than the flat disks used previously¹⁶ because tubes allow a thinner wall for

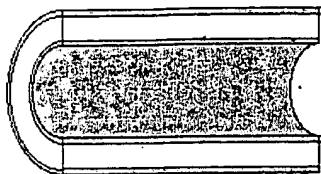


Figure 2. Cutaway diagram of a tubular membrane.

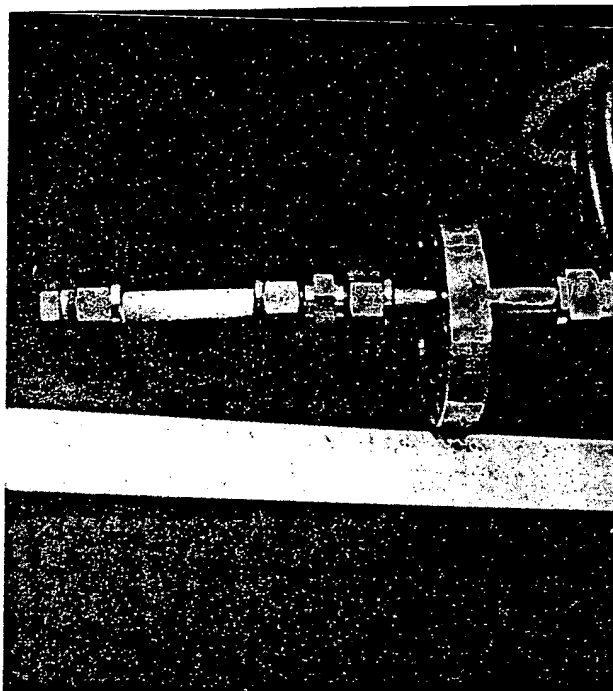


Figure 3. Photograph of a membrane in a Swagelok holder.

a given pressure differential, and thus allow higher hydrogen fluxes. Also, tubular membranes are easily fabricated into large-scale hydrogen extractors using a shell-and-tube heat-exchanger design.

Most of the experiments presented here use tantalum because tantalum showed less hydrogen embrittlement. Niobium is somewhat cheaper and more permeable to hydrogen than tantalum but is more readily embrittled.¹⁶ Several alloys have shown higher hydrogen permeability than these elements and avoid hydrogen embrittlement entirely, but none are as readily available in tube form.

Preparing, Coating, and Evaluating Tubular Membranes

We started with commercial-grade tantalum heat-exchanger tubes $\frac{3}{8}$ in. in diameter in four wall thicknesses (0.054-, 0.037, 0.027, and 0.007 cm) and with a niobium tube ($\frac{3}{8}$ -in.-diameter, 0.034-cm wall). Tube lengths were between 4 and 41 in. The surfaces of these tubes arrive from the manufacturer coated with a layer of oxide and often with a layer of oil. Both of these interfere with the coating process and must be removed in order to make an acceptable membrane. Gross oxide and oil was removed by abrasion and detergent. We then electropolished, hydrided, and applied our electroless palladium coat as described previously.¹⁵ For several of the coated tubes, we used hydrazine as the reducing agent instead of hypophosphate. Hypophosphate was found to deposit palladium-5% phosphorus,^{24,25} and we hoped to find superior performance with a purer palladium coat produced by reducing with hydrazine.

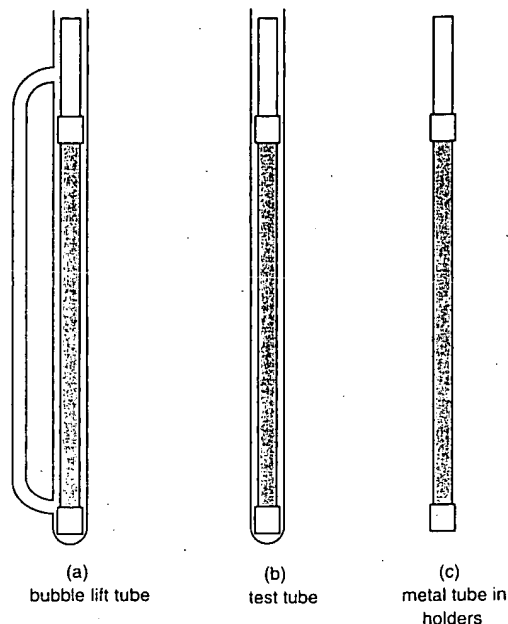


Figure 4. Electroless coating setups.

With several tubes the solution was mixed continuously during plating by performing the plating in a test tube with a side arm (Figure 4a). Here, gas that evolves during coating causes an upward flow of solution, and the side arm allows a return flow once the bubbles leave (gas-lift circulation). We thought such circulation might improve the coat. The rest of the membranes were coated in large test tubes (Figure 4b) and stirred only occasionally. In all, we coated more than 60 tantalum tubes and 20 niobium tubes.

Several membranes were annealed at high pressure (HIPing) by sealing the apparatus exits and pressurizing with 100 psi of argon. Membranes were heated to 500–525 °C and kept this way for several hours or days to see whether higher hydrogen fluxes resulted from an improved bond between the palladium and the substrate. Sawatzki and Ledoux¹⁴ found that annealing for 4 h at 700 °C improved hydrogen removal from a palladium-coated zirconium tube, presumably because of increased bonding.

Permeability and Durability Measurement

The permeabilities of the palladium-coated metal membranes were studied using the apparatus shown in Figures 5 and 6. The membranes were reliably sealed into the apparatus via swageloks (Figure 5). We use graphite ferrules to allow the membrane to swell without stress embrittlement or leaks.

Impure hydrogen—gas, or a mixture of hydrogen and argon, enters the apparatus as indicated by the arrows in Figures 5 and 6. The gases travel up the outside of the module while being heated to operation temperature, they then flow down the inside of the apparatus and contact the membrane. Much of the hydrogen permeates the membrane, and the rest exits along with the argon or impurities. We measure the flow rate of hydrogen through the membrane and the gas pressures at the inlet and exits (Figure 6). From this and the membrane area, we calculate the effective permeance of the membrane via eq 5. The total membrane resistance is then the inverse of the permeance and equals the sum of mass-transfer resistances in the palladium, in the tantalum, in the interface (if any), and in the

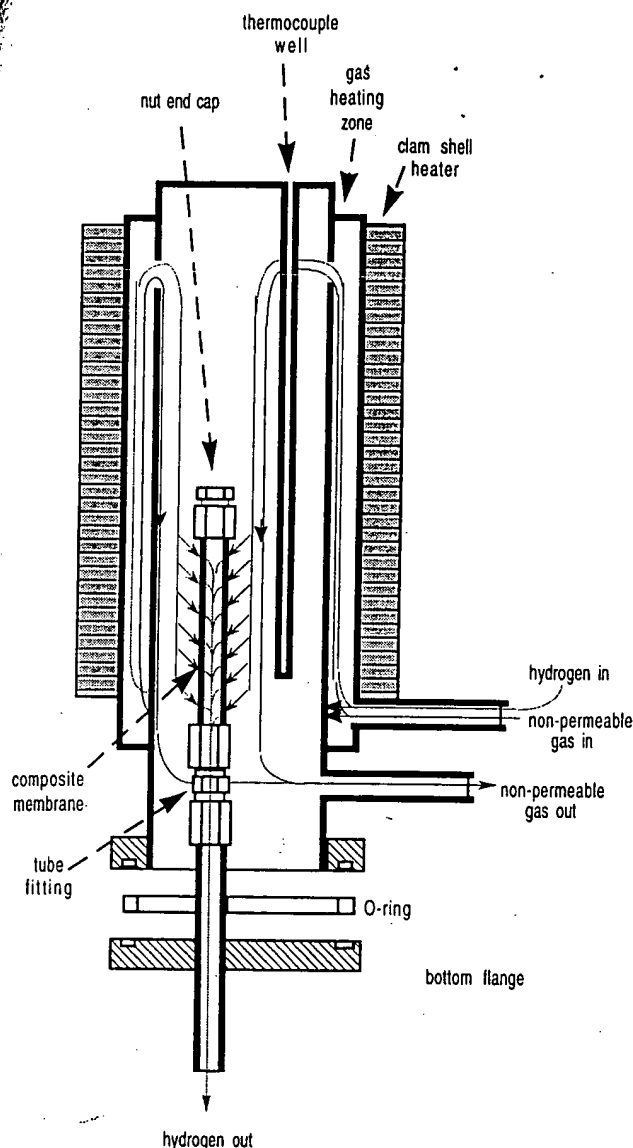


Figure 5. Membrane permeation apparatus.

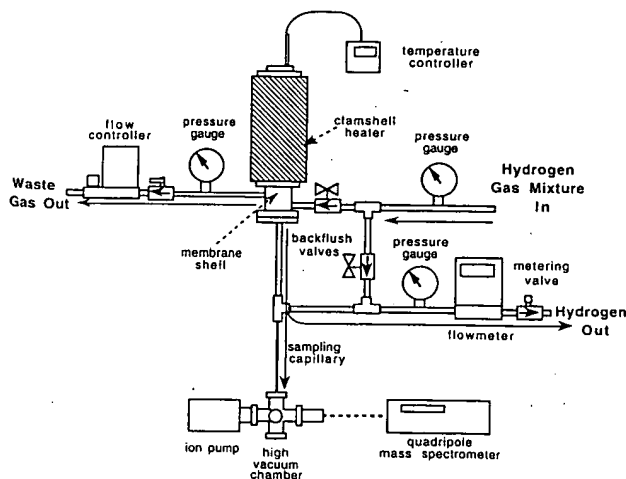


Figure 6. Membrane test apparatus showing flows.

flowing gas stream. The effective membrane permeability is calculated from the permeance and thickness via eq 5.

Durability tests involved measuring the permeation flux continuously for several weeks. During durability testing membranes were given weekly backflushes with hydrogen to drive off coke and other contamination that

may have agglomerated on the upstream membrane surface. Backflushing was done by reversing the hydrogen flux through the membrane.

As with our earlier experiments,¹⁰ we regularly check for leaks by analyzing the output hydrogen purity, here using an on-line mass spectrometer (Figure 6). Any sign of argon in the output is evidence of a leak, and we shut down. Except when testing for leaks, the membrane is run with Matheson 99.8% pure hydrogen as a feed and 98% hydrogen (approximately) as a purge. This purity was chosen to minimize gas-phase mass-transfer resistance, while getting an industrially-significant measure of the permeance. Gas-phase mass-transfer resistance can be very large with these membranes because of the very high hydrogen fluxes.

Electron Microscopy, X-ray, and Auger Spectroscopy

Electron microscopic and X-ray examination of the coat was used extensively because it gave an excellent image of coat thickness and uniformity at the magnifications of interest, about 5000 \times . A combination of Auger and X-ray spectroscopy was used to determine elemental compositions of the coat and of the interface. Auger spectroscopy was used to determine that there were no foreign elements at the surfaces or interfaces, but because of the small spot size, it is easily confused by oxygen or water that adheres to the sample surface during mounting. X-ray spectroscopy scans a much larger volume, making it more accurate for studying coat composition, but it is insensitive to all but the grossest interdiffusion effects, and it is blind to oxygen, nitrogen, and carbon contaminants.

Results: Solution Coating and Stirring

We coated several 18 in. long membranes in the simple test tubes (Figure 4b), stirring occasionally by hand. We coated several others (including the largest membrane, 41 in. long) using gas-lift solution circulation (Figure 4a). In either apparatus a 1–3 μm palladium coat requires from 4 to 12 h. We could detect no improvement in coat quality from gas-lift circulation, and since this technique is cumbersome, we recommend using simple test tubes.

The coat formed more readily using hydrazine as the reducing agent instead of hypophosphate. The composition of membranes using Auger spectrometry showed that the Pd coats produced using hypophosphate contained 5% phosphorus impurity and showed some metallic interdiffusion at 420 $^{\circ}\text{C}$. The newer hydrazine-based coats showed no detectable impurities and no clear sign of interdiffusion. Figure 7 suggests that the transport resistance is somewhat lower with hydrazine as well.

After long periods of operation, especially at high temperatures, the palladium surface tended to turn darker than at first. Auger, electron microscope and X-ray analysis comparing membranes before and after operation showed no clear sign of interdiffusion but showed a surface morphological change. Apparently, we are making "palladium black", the palladium equivalent of platinum-black catalyst. This increased surface roughness may explain the observation that flux increases during the first few hours of operation and eventually decreases (see below). Figure 3 shows a membrane after 31 days of operation at 420 $^{\circ}\text{C}$; surface darkening is seen at the tube end near the ferrule. We

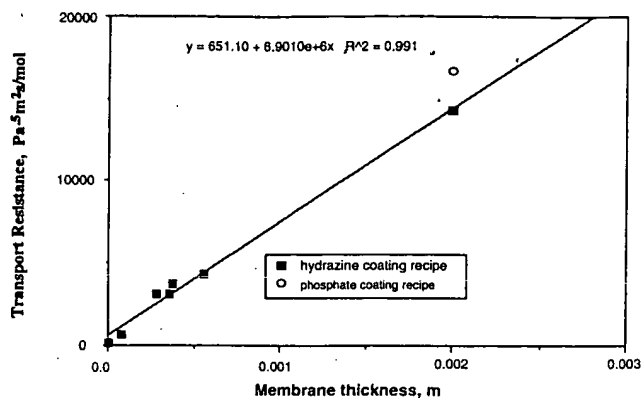


Figure 7. Transport resistance in palladium-coated Ta membranes at 420 °C; two coating recipes.

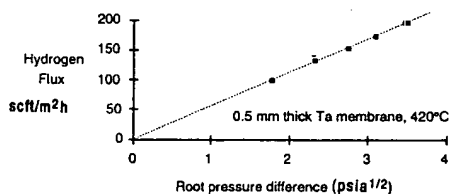


Figure 8. Hydrogen flux vs. root pressure difference.

suspect that surface darkening is caused by defect migration from below. These defects may have been caused by expansion of the palladium or refractory metal during hydrogen absorption.²⁷ We could test this hypothesis by replacing the pure metal palladium and substrates with less defect-prone alloys or by charging the substrate with different amounts of hydrogen before coating.

When observed with Auger spectroscopy, all coats showed significant surface carbon and oxygen. This contamination is probably due to exposure to the atmosphere during sample mounting and is probably not representative of the permeation environment.

Membrane Permeability

Figure 7 plots the effective resistance of several membranes as a function of refractory metal thickness. As expected from eq 6, resistance increases in proportion to membrane thickness, but Figure 7 also suggests that transport resistance is somewhat higher with the older phosphate recipe than with the newer recipe. A positive intercept is expected in this plot, representing transport resistance through the palladium coat, surfaces, and interfaces. The correlation coefficient for the linear fit is 0.991, including only membranes coated by the newer recipe.

The slope of the line in Figure 7 should be inversely proportional to the tantalum permeability for any fixed surface or palladium transport resistance (eq 3), i.e., $\mathcal{P}_M = 1/(\Delta R_M/\Delta \delta_M)$. Surface and fixed palladium-layer resistances affect only the intercept of this line, assuming only that they remain constant throughout. Thus at 420 °C, the average permeability of tantalum equals $1/6.901 \times 10^6$ or 1.45×10^{-7} mol/m s Pa^{1/2}. This value is in close agreement with Figure 1. Our previously reported value for the permeability of tantalum was 30% lower,¹⁶ but this value was not corrected for surface resistance.

Figure 8 shows the hydrogen flux with a thick-walled palladium-tantalum membrane as a function of pressure differential at 420 °C. The upstream pressures ranged from 1 to 3 atm, and downstream pressures ranged from

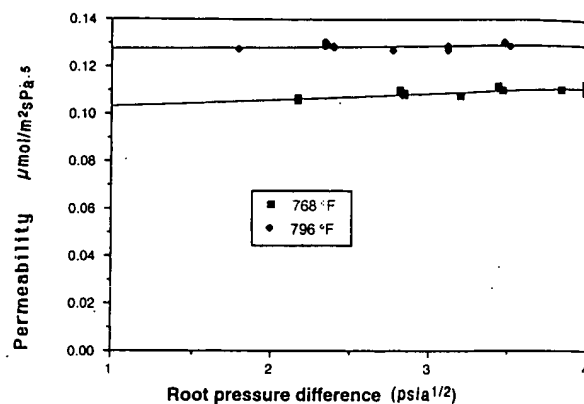


Figure 9. Tantalum membrane permeability vs temperature and pressure.

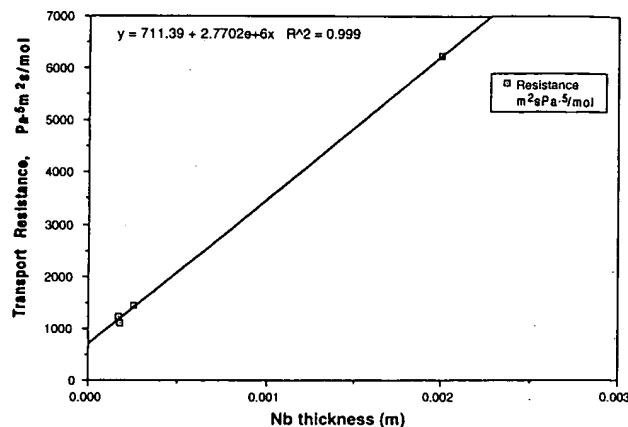


Figure 10. Transport resistance in Nb-based membranes vs membrane thickness.

near vacuum to about 1.5 atm. For all driving pressures studied, flux is nearly proportional to pressure difference to the ¹/₂ power, agreeing with eq 3. The average effective permeability here is 1.2×10^{-7} , somewhat lower than the above because of resistance in the palladium coat and at the palladium surfaces. Still this is 10 times higher than the permeability of palladium alloys at this temperature, about 1.2×10^{-8} mol/m s Pa^{1/2}. Even with thin-walled palladium membranes, the flux is about ¹/₅ the values in Figure 8.

Figure 9 shows the effective permeability of a palladium-coated tantalum membrane as a function of pressure at two temperatures. At both temperatures, it appears that permeability is fairly independent of hydrogen pressure. This is not to say that D_M and K_S are pressure-independent, only that the product of D_M and K_S varies only weakly with H concentration at these temperatures. The permeability is seen to increase with temperature, contrary to the prediction in Figure 1 but in agreement with our previous findings.¹⁹

Niobium Membranes

Niobium heat-exchanger tubes up to 18 in. long were coated with palladium using the same techniques used for the tantalum tubes above. The transport resistance with these membranes is shown in Figure 10. As with tantalum, transport resistance in Nb-based membranes increases linearly with thickness in accordance with eq 5. The intercept resistance in Figure 10 is higher than with tantalum (Figure 7). This higher intercept with niobium may reflect surface resistances or may represent a poorer coating technique. The average permeability in niobium, determined from the slope of the line

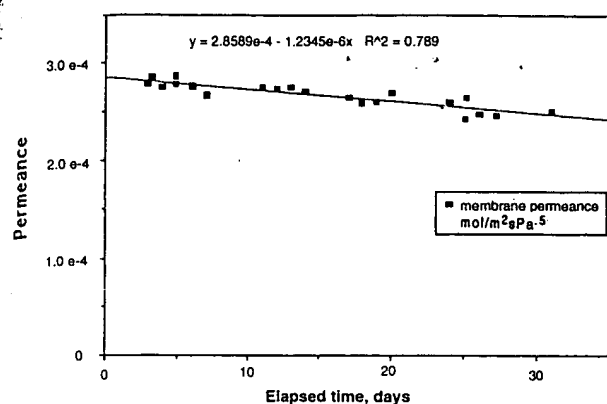


Figure 11. Permeance of a palladium-coated tantalum membrane run for 31 days at 420 °C with weekly backflushes.

as above, is $3.6 \times 10^{-7} \text{ mol/m s Pa}^{1/2}$. This is $2\frac{1}{2}$ times the permeability of tantalum and is almost identical to the value measured using thick niobium disks.¹⁶ This value, however, is about half the prediction in Figure 1.

The maximum permeance of our Nb-based membranes was $0.0011 \text{ mol/m}^2 \text{ s Pa}^{1/2}$, 75% that of the thinnest-wall tantalum-based membranes. This lower permeance could be improved if thinner walled niobium were used; the thinnest-wall niobium membranes were 0.15 mm thick, twice the thinnest-wall tantalum membranes.

Membrane Durability

Commercial membranes should last a few months to a few years in service with only minimal loss of flux. To test our membrane's durability, we measured the flux in several membranes for periods up to 31 days.

A tantalum-based membrane that was run for 31 days at 420 °C is shown in Figure 3. It looks like new except for a slight darkening near the upper ferrule as discussed above. Figure 11 shows that the permeance of this membrane decreases with time, decreasing about 15% over 31 days of operation. The decrease is approximately linear with time, varying only slightly on a daily basis, presumably due to variations in gauge readings, atmospheric pressure, and the effect of weekly backflushes. Weekly backflushing with hydrogen is found to increase the flux by a few percent. Membranes coated using the older phosphate recipe deteriorated somewhat faster, possibly because of the difficulty in getting a good coat.

Hydrogen embrittlement was a serious problem with tantalum and niobium membranes. The minimum temperature for tantalum membranes was 350 °C, dictated by the need to avoid embrittlement cracking. The minimum temperature for niobium membranes was 420 °C for the same reason. Cracking is also affected by hydrogen pressure, metal annealing, and thickness and by the tightness of the ferrules.

Discussion

The flux with these membranes is about that predicted from theory and earlier experiments but increases with temperature, contrary to our simple expectations for Ta and Nb. Two effects may cause this behavior. First, the palladium coat adds a resistance and this resistance decreases with increasing temperature. Further, as temperatures increase, the hydrogen content decreases and this increases diffusion rates by

increasing the number of vacant sites next to the hydrogen atoms.²⁰ These two effects could cause the rise in effective membrane permeability for the pressures and Pd thicknesses studied.

The thinnest membranes, made from 0.07 mm wall tantalum tubes, show transport resistance of $700 \text{ m}^2 \text{ s Pa}^{1/2}/\text{mol}$ (permeances of $0.00147 \text{ mol/m}^2 \text{ s Pa}^{1/2}$). Fluxes with such membranes are higher than those with any other nonporous membrane that we know of and continue to increase with decreasing tantalum thickness. This suggests that the major transport resistance is in the substrate, at least for the membrane thicknesses studied.

The flux is higher than with the commercial polymeric membranes, but the cost seems higher as well, currently this is about \$500/ft² as compared with \$200/ft² for polymers.³¹ Thus, flux and price are in the range for economical application. Scaleup and fabrication do not seem to be a serious problem since the coating methods are simple. The membranes are attached by standard swageloks. The 15% decrease in flux for 31 days is a serious concern, though, since the root causes are not clear at this stage.

Membrane life will have to be extended to 1 year or so before they are ready for commercial use. If transport resistance adds at the steady rate of 15%/month, as appears from Figure 11, the membrane flux would fall below 50% in 6–7 months. We have tried several "cures" at this stage, and none has worked completely. Presuming that the cause was small amounts of impurity concentrating at the metal surface (fouling), we tried backflushes as described above. This helped but did not completely erase the deterioration, possibly a longer backflush is needed. Alternatively, if the observed morphological changes caused deterioration, maybe a low-swelling alloy would deteriorate slower than the pure metals used here. Alternatively, deterioration may be due to interdiffusion of the palladium and substrate as suggested by Edlund.²⁶ This is the "best result" since interdiffusion would tend to slow on its own as the interdiffusion layer grew. Thus, the membrane tested in Figure 11 might be expected to operate for years before the flux dropped 50%. Edlund et al.²⁶ found evidence for intermetallic interdiffusion at 700 °C, but the flux decrease in Figure 11 looks too steady for this explanation. Deterioration shows no slowing as the interdiffusion zone increases, but our experiments were of short duration. Longer term experiments will show whether interdiffusion is the cause.

In a preliminary experiment we were able to reverse this deterioration completely by replacing the palladium surface with fresh palladium. More experiments are being conducted in this area.

Sample Design, Hydrogen Extraction from Hydrotreater Off-Gas

Hydrogen is used in petrochemical plants for hydrodesulfurization and for methanol and ammonia synthesis. Additional hydrogen has a value in such plants because it reduces plant energy costs and allows more flexible operation, e.g., it allows production of a "reformulated" gasoline that maintains current octane levels but has fewer aromatics (aromatics are carcinogenic, polluting components of gasoline). A common route to reformulated gasoline is to reduce the flow and temperatures in reformer units while increasing the flow and temperature in Catcracker fluidized-bed reactors.

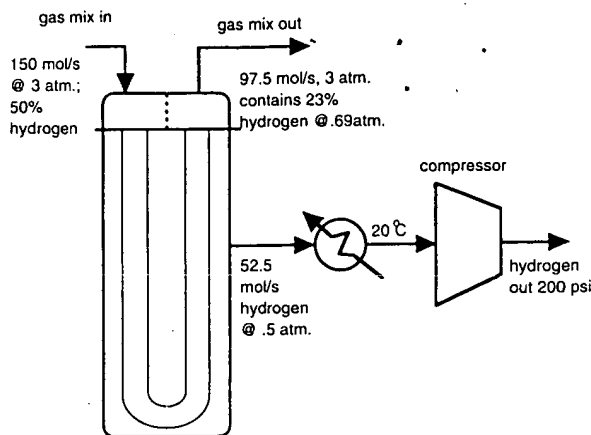


Figure 12. Setup for hydrogen removal from hydrotreater off-gas.

This change reduces the amount of reformer hydrogen available for hydrodesulfurization and resid upgrading, so this route requires a source of additional hydrogen. Depending on the plant, pure hydrogen has a chemical value about \$2.00/kg mol (\$0.002/g mol) above its fuel value.^{26,27}

We will consider a modestly large stream of hydrotreater off-gas: 10 000 000 scf/day at 3 atm, containing 50% hydrogen mixed with methane, ethane, water, and CO₂. Refineries produce and burn such streams as "fuel gas" because the low-pressure hydrogen is too expensive to recover. We will recover 70% of this hydrogen using a metal membrane-based extractor in the shape of a shell and tube heat exchanger (Figure 12). The gas mixture flows through the tubes, while the hydrogen is recovered from the shell. The double-pass, vertical-standing design minimizes problems of metal expansion and membrane support. In SI units, the flow is 150 mol/s, with hydrogen making up 75 mol/s; if 70% is recovered, this is 52.5 mol/s (3.5 MMscf/day).

For a benchmark design, consider 420 °C operation, using 1 cm diameter tubes of our best current palladium-covered tantalum. These tubes have a permeance of 0.001 47 mol/m² s Pa^{1/2}, are strong enough for the pressures and temperatures needed, and, because of their large diameter, add minimal gas-phase pressure drop. Still, the hydrogen pressure in the shell must be lower than the minimum hydrogen partial pressure in the tubes since this pressure difference drives the extraction. The minimum hydrogen pressure in the tubes is:

$$H_2 \text{ partial pressure} = \frac{(3 \text{ atm}) \times (22.5 \text{ mol/s unrecovered } H_2)}{97.5 \text{ exiting mol/s}} = 0.69 \text{ atm} \quad (7)$$

For design purposes, pick a hydrogen shell pressure of half this, 0.35 atm. (It is generally recognized that polymer membranes are not economical at such low-pressure gradients.)

The membrane surface area is calculated from the permeance, 0.001 47 mol/m² s Pa^{1/2}:

$$\text{flux, } N = \frac{52.5 \text{ mol/s}}{\text{area}} = P_{up}^{1/2} - P_{dn}^{1/2} (\text{permeance}) \quad (8)$$

where P_{up} is the average hydrogen partial pressure in

the tube, P_{dn} is the hydrogen pressure in the shell, and 52.5 mol/s is the design load. P_{up} varies between 1.5 atm at the tube inlet and 0.69 atm at the tube outlet, but for eq 8, let us use the geometric average 1.0 atm, or 100 000 Pa in SI units. The downstream hydrogen pressure is 0.35 atm, or 35 000 Pa. The flux is thus

$$N = (316.2 - 187.1 \text{ Pa}^{1/2})(0.00147) = 0.190 \text{ mol/m}^2 \text{ s}$$

From eq 7, the membrane area is

$$A = (52.5 \text{ mol/s}) / (0.190 \text{ mol/m}^2 \text{ s}) = 276 \text{ m}^2$$

For an extractor of this area, the shell could be 5.5 m long, containing doubled tubes 10 m long. Since each 1 cm diameter × 10 m tube has a surface area of 0.314 m², the extractor will use 880 tubes for a total tube length of 8800 m, or 27 500 ft. The shell diameter for this number of tubes would be about 1 m.

A series of intercooled compressors is now chosen to bring the hydrogen to 200 psi for general plant use. Steam sparging is a cheaper alternative for the first stage of hydrogen compression, but it contaminates the hydrogen with water vapor.

Economics of Hydrogen Recovery with This Extractor

The adiabatic pumping cost is estimated as the isothermal compression work at 400 K, an average gas temperature assuming inefficient intercooling.

$$W = RT \ln(P_f/P_i) = 8.314 \times 400 \times 3.660 = 12 \text{ kJ/mol} \quad (9)$$

At 7.5¢/kwh this operating cost is 0.025¢/mol.

The total equipment cost is now calculated from the cost of tubes, shell, pumps, etc. Large runs of uncoated tantalum tubes are priced at about \$15/ft. Coating 1 μm of Pd on each side is estimated to add an additional \$5/ft, and thus the membranes cost about \$20/ft, or 0.55 M\$ total. Added to this are the purchase cost of the shell, fabrication, control, and heat exchanger, an additional \$200 000. The projected capital cost excluding pumps is thus 0.75 M\$, which is increased to 1.25 M\$ including the price of rotary vane pumps.

This capital cost must be compared to the value of the recovered hydrogen minus operating costs. Assuming the hydrogen is worth 0.2¢/mol more than its fuel value and operating costs are 0.025¢/mol as calculated above, operating profit is

$$(52.5 \text{ [mol/s]}) \times (0.002 - 0.00025 \text{ [$/mol]}) \times (3.15 \times 10^7 \text{ [s/yr]}) = 2.9 \text{ M$/yr}$$

Given the capital cost of 1.25 M\$, the payback period is less than 5 months, which is excellent. The calculations can be redone using our current membrane cost, \$45/ft, and the payback period is found to be less than 8 months, which is still excellent. Optimization should result in improved economics.

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Literature Cited

- (1) Armor, J. N. Catalysis with Permselective Inorganic Membranes. *Appl. Catal.* 1992, 49, 1-25. Also: Armor, J. N. *CHEMTECH* 1992, 22, 557-563.

- (2) Phillpott, J.; Coupland, D. R. Metal Membranes for Hydrogen Diffusion and Catalysis. *Hydrogen Effects in Catalysis*, Paal, Z., Menon, P. G., Eds.; Marcel Dekker: New York, 1988; pp 679-694.
- (3) Tsotis, T. T.; Champagnie, A. M.; Vasileiadis, S. P.; Zaika, Z. D.; Minet, R. G. The Enhancement of Reaction Yield through High Temperature Membrane Reactors. *Sep. Sci. Technol.* **1993**, *28*, 397-422.
- (4) Makrides, A. C.; Wright, M. A.; Jewett, D. N. Separation of Hydrogen by Permeation. U.S. Patent 3,350,846, Nov 7, 1967.
- (5) Hsu, C.; Buxbaum, R. E. *J. Electrochem. Soc.* **1985**, *132*, 2419.
- (6) Hsu, C.; Buxbaum, R. E. *J. Nucl. Mater.* **1986**, *141-143*, 238.
- (7) Buxbaum, R. E. *Sep. Sci. Technol.* **1983**, *18*, 1251.
- (8) Perng, T. P.; Altstetter, C. J. *Metall. Trans.* **1986**, *17A*, 2086-2090.
- (9) Hill, E. F. Feasibility Study: Removal of Tritium from Sodium During the MDEC Process by Oxidative Diffusion. Argonne West, DOE N707T1830035, 1982.
- (10) Buxbaum, R. E.; Hsu, P. C. *J. Nucl. Mater.* **1992**, *189*, 183-192.
- (11) Steward, S. A. Review of Hydrogen Isotope Permeability through Materials. Lawrence Livermore National Laboratory Report, UCRL-53441, 1983.
- (12) Buxbaum, R. E. Composite Metal Membranes for Hydrogen Extraction. U.S. Patent 5,108,724, Dec 15, 1991.
- (13) Pick, M. A. *Proceedings NATO Institute on Metal Hydrides*; Bambakidis, G., Ed.; Plenum Press: New York, 1981; pp 329-343. Review works by: Pick, M. A.; Davenport, J. W.; Strongin, M.; Dienes, G. J. *Phys. Rev. Lett.* **1979**, *43*, 286-289. Pick, M. A.; Greene, M. G.; Strongin, M. *J. Less-Common Met.* **1980**, *73*, 89.
- (14) Sawatzki, A.; Ledoux, G. A. The Use of Palladium to Remove Hydrogen from Zirconium. Presented at the 2nd International Congress on Hydrogen in Metals, Paris, France, 1977.
- (15) Buxbaum, R. E.; Hsu, P. C. Method for Plating Palladium. U.S. Patent 5,149,420, issued Sep 22, 1992.
- (16) Buxbaum, R. E.; Marker, T. L. Hydrogen Transport in Nonporous membranes of Palladium-coated Niobium, Tantalum, and Vanadium. *J. Membr. Sci.* **1993**, *89*, 29-38.
- (17) Kleiner, J. E.; Sevilla, E. H.; Cotts, R. M. Diffusion of Hydrogen in α -VH_x. *Phys. Rev. B* **1986**, *33*, 6662.
- (18) Hemplemann, R. Diffusion of Hydrogen in Metals. *J. Less-Common Met.* **1984**, *101*, 69-97. All of this special volume concerns hydrogen in metals.
- (19) Amano, M.; Komaski, M.; Nishimura, C. Hydrogen Permeation Characteristics of Palladium Plated V-Ni Alloy Membranes. *J. Less-Common Met.* **1991**, *172-174*, 727-731.
- (20) Peterson, D. T.; Jensen, C. L. Diffusion of Hydrogen in Niobium-Tantalum Alloys at 296 K. *Metall. Trans. A* **1980**, *11A*, 627-631.
- (21) Zarchy, A. S. Limitations on Hydrogenic Gas Transport at Ultra-Low Pressures. Ph.D. Thesis, Princeton University, 1978, University Microfilms, pp 10-19.
- (22) Fukada, S.; Nakahara, T.; Mitsuishi, N. *J. Nucl. Mater.* **1990**, *171*, 399-407.
- (23) Kumar, V.; Bennemann, K. H. Electronic Structure of Transition Metal-Transition Metal Interfaces: Pd on Nb(110). *Phys. Rev. B* **1983**, *28*, 3138-3149.
- (24) Govind, R.; Atnoor, S. Development of a Composite Palladium Membrane for Selective Hydrogen Separation at High Temperature. *Ind. Eng. Chem. Res.* **1991**, *30*, 157-158. See also: Itoh, N.; Govind, R. Development of a Novel Oxidative Palladium Membrane Reactor. *AIChE Symp. Ser.* **1989**, *268*, 10-17. Ilias, S.; Govind, R. Development of High Temperature Membranes for Membrane Reactors, an Overview. *AIChE Symp. Ser.* **1989**, *268*, 18-25.
- (25) Paunovic, M. *Proc. Symp. Electroless Deposition Met. Alloys* **1988**, 252-258.
- (26) Edlund, D. Metal Membranes for High Temperature Gas Separations. *Proceedings of the 1990 Membrane Conference*, Business Communications, Norwalk, CT, 1991; p 77.
- (27) Shu, J.; Grandjean, B. P. A.; VanNeste, A.; Kaliaguine, S. Catalytic Palladium-Based Membrane Reactors: A Review. *Can J. Chem. Eng.* **1991**, *69*, 1036-1060.
- (28) Uemiyu, S.; Kude, Y.; Sugino, K.; Sato, N.; Matuda, T.; Kikuchi, E. A Palladium-Porous glass Composite Membrane for Hydrogen Separation. *Chem. Lett.* **1988**, *10*, 1687-1690.
- (29) Collins, J. P.; Way, J. D. Preparation and Characterization of a Composite Palladium-Ceramic Membrane. *Ind. Eng. Chem. Res.* **1993**, *32*, 3006-3013.
- (30) Ali, J. K.; Newson, E. J.; Rippin, D. W. T. Exceeding Equilibrium Conversion with a Catalytic Membrane Reactor for the Dehydrogenation of Methylcyclohexane. *Chem. Eng. Sci.* **1994**, *49*, 2129-2134.
- (31) Johnson, H. E.; Schulman, B. L. Assessment of the Potential for Reinery Applications of Inorganic Membrane Technology—an Identification and Screening Analysis. U.S. DOE Report, DOE/FE-60680-H3, May 1993.

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